

Ferroelectric thermal phase transition and polarization precursor dynamics in $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ tungsten bronze type oxides

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Abstract

Polycrystals of $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (CBN) tungsten bronze type oxides have been prepared and their structural, dielectric, and thermal properties have been investigated. It was found that CBN alloys with ferroelectric tetragonal tungsten bronze structure were only available in a composition range of $0.19 \leq x \leq 0.32$. It was also showed that CBN can be classified as a ferroelectric with a first-order thermal phase transition showing polarization precursor dynamics before transition into ferroelectric phase, in sharp contrast to an isostructural alloy $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) that shows typical relaxor behaviors. The local polarizations were found to grow exponentially within the paraelectric mother phase in a large temperature range of $T_c < T < T_c + 88 \sim 140$ K on cooling. Furthermore, a phase diagram was established for CBN ferroelectric alloys. These findings may get an insight into the true nature of ferroelectric phase transition in this potential electro-optic material.

I. INTRODUCTON

There are increasing interests in seeking novel electro-optic materials analogous to the famous $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN, $0.32 \leq x \leq 0.75$) that belongs to the $(\text{A}_1)_2(\text{A}_2)_4(\text{B}_1)_2(\text{B}_2)_8\text{O}_{30}$ tetragonal tungsten bronze (TTB) structure with the non-centrosymmetry of P4bm at room temperature (see Fig.1) [1–3] and shows excellent electro-optic and pyroelectric properties [4] and typical relaxor behaviors.[5, 6] Recently, $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (CBN, $0.2 \leq x \leq 0.4$) single crystals have received considerable critical attention due to their excellent electro-optic properties and higher working temperature in comparison with SBN.[7–11] The ferroelectricity of CBN is first discovered by Smolenskii et al..[12] CBN alloys also have the ferroelectric TTB structure at room temperature, however, contrary to Sr in SBN where Sr ions randomly occupy both the two large A_1 and A_2 sites in the tungsten bronze framework of NbO_6 octahedra, smaller Ca ions in CBN only occupy the A_1 sites in the structure. It has been demonstrated experimentally that smaller A_1 site is almost exclusively occupied by Ca while larger A_2 site is predominately by Ba in CBN single crystal with congruent melting composition ($x=0.28$).[13, 14] In ferroelectric CBN alloys, niobium atoms are displaced from the centers of their coordination polyhedra and shifted along the tetragonal c -axis, which is considered to be the origin of spontaneous electric polarization.[3, 15]

Currently, most of investigations on CBN alloys are focused on the crystal growth[7, 11], dielectric,[10, 16] ferroelectric,[10] optic,[17–19] and elastic [20–23] properties of CBN single crystal with congruent melting composition $x=0.28$. Despite these investigations on CBN, there is still a lack of full understanding on the basic issues in CBN alloys. One important problem is that CBN alloys are relaxors (such as their isostructural compounds SBN alloys[6, 24–26]), which is characterized by a broad peak of dielectric susceptibility with strong frequency dispersion in the radio frequency over a large temperature range [26–29] and smear ferroelectric phase transition[28, 30] without an obvious heat capacity peak,[31] or they are ferroelectrics (such as the normal ferroelectric BaTiO_3), which have a well-defined para-ferroelectric thermal phase transition at Curie point T_c [32] but show polarization precursor dynamics before transition into the ferroelectric phase.[33–38] Since CBN is an isostructural compound of SBN that typical relaxor phenomena have been clearly demonstrated,[25, 26] it is naturally expected that CBN should show the relaxor behaviors such as a broad peak of dielectric susceptibility with strong frequency dispersion due to

the dynamics of polar-nano-regions (PNRs) occurring in the paraelectric mother phase. Following this scenario, several attempts have been made to confirm the relaxor behaviors in CBN.[20–23] From the investigations on lattice strain and thermal expansion of CBN single crystal with congruent melting composition $x=0.28$, Pandey et al. found the deviation from the linear temperature dependence of lattice strain and the anomalous thermal expansion in this single crystal.[20] They attribute these anomalous elastic behaviors to the relaxor phenomena occurring in CBN crystal. They further suggest Burns temperature [33] T_B to be 1100 K, which characterizes the initiation of dynamic PNRs, and the intermediate temperature T^* to be 800 K, which indicates the beginning of PNRs freezing,[39, 40] for CBN with $x = 0.28$. [20] On the other hand, in a recent Brillouin scattering study, T_B and T^* are proposed to be approximately 790 K and 640 K, respectively, for CBN with the same composition.[23] The difference in T_B and T^* values estimated by different techniques for a same compound is surprisingly large. Apparently, the existence and exact values of T_B and T^* in CBN need to be clarified in further investigations.

It should be noticed that the existence of T_B and T^* is not the characteristic properties of relaxor. In a normal ferroelectric such as BaTiO_3 , the existence of these two characteristic temperatures have been clearly demonstrated.[33, 37] In early investigations, Burns et al.[33] have demonstrated that the temperature dependence of the optic index of refraction, $n(T)$, deviates from the high temperature extrapolated value between T_c and T_c+180 K in the paraelectric phase of BaTiO_3 crystal. This deviation is commonly accepted to be due to the local polarization precursor dynamics before the para-ferroelectric phase transition in BaTiO_3 , thus the temperature where this deviation occurs is generally called as Burns temperature T_B , which is widely used to characterize the appearance of PNRs in the paraelectric phase of ferroelectric or relaxor. In addition to the optical measurements,[33, 35, 38] various other experiments such as pulsed X-Ray laser measurements,[34, 41] acoustic emission[37] and Brillouin light scattering[36] all show the existence of local polarization in BaTiO_3 before transition into the ferroelectric phase. Theoretically, it has been proposed that local dynamical precursor domains are common to perovskite ferroelectrics, and these polar domains grow upon approaching T_c to coalesce into a homogeneously polarized state at T_c . [42, 43] Similarly, PNRs develop from T_B in relaxor, and cause the very strong frequency dispersion of dielectric susceptibility. In contrast to relaxor, precursor domains in the perovskite ferroelectric such as BaTiO_3 do not need to give rise to a frequency-dependent dielectric response

in the radio frequency.[43]

Furthermore, a sharp peak of heat capacity has been observed at the para-ferroelectric phase transition in CBN crystal with $x = 0.311$. [9] Also, in the dielectric measurements on CBN single crystal with congruent melting composition $x=0.28$, it seems that the para-ferroelectric phase transition temperature is not dependent on frequency.[10] All these findings in CBN are in sharp contrast to the characteristic properties of relaxor such as smear phase transition [28, 30] without an evident heat capacity peak,[31] and very strong frequency dependence of dielectric responses in the radio frequency around a temperature, T_m , where the maximum of dielectric response occurs. These results suggest that CBN alloys may be classified as a ferroelectric with thermal phase transition associating with polarization precursor dynamics rather than a relaxor.

In this study, we firstly determined the solid solution limit of CBN ferroelectric alloys. We then investigated the para-ferroelectric phase transition in these alloys by the dielectric measurements and the differential scanning calorimetry (DSC). Contrary to the relaxor picture what have been expected in previous investigations,[20–22] we clearly demonstrated that CBN alloys can be classified as ferroelectrics with a first-order thermal phase transition associating with precursor dynamics over a large temperature range above T_c such as BaTiO_3 . [33, 35, 38] We also found that the local polarizations grown exponentially for a temperature range of $T_c < T < T_c + 88 \sim 140$ K on cooling in CBN alloys. These findings are of benefit in understanding the nature of ferroelectric phase transition in CBN crystals that are currently developed for the electro-optic applications.

II. EXPERIMENTAL

We used a conventional solid-state reaction method to prepare CBN polycrystals, which allows us to easily control composition of CBN samples. To obtain dense ceramics for electrical measurements, CBN ceramics samples were fired 3 hours at a temperature of 1693 K (approximately 50 K lower than its melting point[9]). This firing allows us to obtain ceramics samples with a relative density larger than 93 % of the density calculated by the structural data. Grain size in the ceramics samples was observed to be approximately $10\mu\text{m} \sim 50\mu\text{m}$ by Scanning Electron Microscopy. To determine the solid solution limit, ceramics samples with composition of $0.15 \leq x \leq 0.40$ were prepared and investigated.

Phase formation and lattice parameters of CBN were determined by powder X-ray diffraction technique using the Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Ceramics samples coated with gold electrode were used for the dielectric measurements by using Agilent 4980A LCR meter. The dielectric measurements were carried out in a temperature range of 300 K - 870 K with a heating/cooling rate of 2 K/min for the exact determination of ferroelectric transition temperature in CBN alloys. To confirm the thermal phase transition in CBN, we also performed DSC measurements by using SII DSC6220 differential scanning calorimetry.

III. RESULTS AND DISCUSSIONS

A. Ferroelectric solid solution limit and lattice parameters

To determine the solid solution limit of CBN ferroelectric alloys, we have prepared the samples with composition ranging from $x = 0.15$ to $x = 0.40$ at a firing temperature of 1693 K, and examined the phase formation by powder x-ray diffractions. As shown in Fig.2, single phase of CBN with ferroelectric TTB structure is only available in a composition range of $0.19 \leq x \leq 0.32$, beyond which CaNb_2O_6 - or BaNb_2O_6 -type phase with non-ferroelectric orthorhombic structure was found in the compounds. The change of lattice parameters or Curie temperature with composition also show a saturation for $x < 0.19$ or $x > 0.32$. These facts indicate that single phase of CBN ferroelectric alloys is available only in a composition range of $0.19 \leq x \leq 0.32$.

The lattice parameters of CBN alloys at room temperature were then determined by the method of least squares using twelve reflections with $2\theta > 50$ degree. The results are shown in Fig.3. In CBN alloys with ferroelectric TTB structure, a -axis lattice is nearly unchanged with composition within the error range. In contrast, the polar c -axis lattice is shorten with an increase in Ca concentration, which results in a similar decrease of unit cell volume. This result is expectable because the ionic radii of Ca and Ba are 1.34 \AA and 1.61 \AA , [44] respectively, and Ca has a smaller ionic radius. In spite of the large change in composition x ($\Delta x = 0.13$), the corresponding change in the unit cell volume is surprisingly small (approximately 0.65%). This situation is different significantly from the case of substitution of Ca for Ba in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ perovskite oxides, which shows an approximate 3.5%-reduction in the unit cell volume at a same level of Ca-substitution.[32] This fact seems to suggest that

the stacking structure in TTB-type CBN crystal is mainly determined by the framework of NbO_6 octahedra as shown in Fig.(1).

B. Thermal phase transition

To investigate the para-ferroelectric phase transition in CBN alloys, we observed the variation of dielectric susceptibility as a function of temperature in a frequency range from 100 Hz to 100 kHz. The results were shown in Fig.4 and Fig.5, respectively. The dielectric loss for lower frequencies (≤ 1 kHz) was large for temperatures higher than approximately 500 K and was not shown here, which is very likely due to the thermal activation of vacancies in the samples. The large dielectric loss made difficult to determine a reliable value of dielectric susceptibility for these low frequencies for the high temperatures. However, as shown in Fig.5, we indeed observed that (1) Curies point is not dependent on frequency ranging from 100 Hz to 100 kHz, and (2) the dielectric susceptibility measured at frequency between 10 KHz and 100 kHz is nearly independent of frequency in the temperature range of 300 K - 870 K. We thus consider that the dielectric susceptibility measured at frequency between 10 KHz and 100 kHz is free from the effects of vacancies and reflects the intrinsic dielectric response of CBN alloys, which will be used in the later analysis. Apparently, the dielectric response with frequency and temperature in CBN alloys is in sharp contrast to that observed in relaxor.[28] Instead, the dielectric behaviors in CBN are similar to those observed in normal ferroelectric such as BaTiO_3 .[32]

The temperature dependence of dielectric susceptibility shown in Fig.5 clearly indicates that the para-ferroelectric phase transition has a thermal hysteresis. Curies points on heating and cooling have different values. The difference of T_c between heating and cooling is 12.4 K for $x = 0.19$ and it increases to 25.2 K for $x = 0.32$. This indicates that the substitution of Ba with Ca in CBN enhances the thermal hysteresis of para-ferroelectric phase transition. On the other hand, this substitution lowers Curies point T_c of CBN alloys as demonstrated clearly in Fig.4.

To further confirm the nature of thermal phase transition in CBN ferroelectric alloys, we also observed the change in enthalpy during the phase transition by the DSC measurements. The results are shown in Fig.6 Although our equipment doesn't allow us to determine the heat capacity of phase transition, we really observed a change in enthalpy during the phase

transition. DSC measurements also clearly indicate that the phase transition has a thermal hysteresis. This result is in good agreements with that observed in the dielectric measurements shown in Fig.4. Our result is also well accorded with that reported for CBN crystal with $x = 0.31$ showing a sharp peak of heat capacity during the phase transition.[9]

All facts showed above indicate that CBN alloys undergo a thermal phase transition. It can be concluded that the para-ferroelectric phase transition in CBN alloys is of first-order and has a thermal hysteresis of 12.4 K to 25.2 K depending on Ca-concentration.

C. Precursor behaviors

In a recent investigation on CBN single crystal with congruent melting composition $x=0.28$, the birefringence has been demonstrated to occur in a temperature region of $T_c < T < T_c + 40\text{K}$. [17] The birefringence of CBN with TTB structure might have arisen due to the anisotropy of polarization fluctuation $\langle P_c^2 \rangle - \langle P_a^2 \rangle$. In this case, the birefringence reads [45, 46]

$$\Delta n = -(n_0^3/2)(g_{11} - g_{12})\langle P^2 \rangle, \quad (1)$$

where g_{11} and g_{12} are the electro-optic coefficients. The occurrence of birefringence provides a direct evidence to the existence of local polarization in the paraelectric phase of CBN crystal.

To get further insights on the polarization precursor dynamics occurring for $T > T_c$, we performed an analysis on the temperature dependence of dielectric susceptibilities of CBN alloys within its solid solution limit. As mentioned in the above section, here, we only used the data obtained at 100 kHz since these data are considered to be free from the effects of vacancies on the dielectric response. As shown in Fig.7(b), the dielectric susceptibility χ' obeys Curie law,

$$\chi' = \pm C/(T - T_0) \text{ for } T < T_c \text{ or } T > T_B, \quad (2)$$

where C is Curie constant and T_0 is Curie-Weiss temperature. Upon cooling, the dielectric susceptibility deviates from Curie law at a characteristic temperature. Since the existence of Burns temperature T_B and the intermediate temperature T^* are not well established for CBN, [20, 23] Here, we tentatively consider this characteristic temperature as Burns temperature T_B . The values of T_B were estimated to be approximately $T_c + 88$ K for $x = 0.19$ and $T_c + 143$ K for $x = 0.32$, respectively, and T_B showed a nearly linear change with

composition as shown in the phase diagram (Fig.10(a)). The fitting parameters obtained from Curie law are summarized in Fig.8. It should be noticed that Curie constant in the paraelectric phase ($T > T_B$) of CBN alloys has a similar magnitude of that of BaTiO₃ single crystal (1.5×10^5 K).[47]

For temperatures higher than T_B , the dielectric susceptibility of CBN alloys exactly follows Curie law, which indicates that the dielectric response in these high temperatures can be considered to be due to the lattice dynamics. However, on cooling, deviation from Curie law was observed from $T \approx T_B$. As mentioned above, this deviation from Curie law of the dielectric susceptibility can be reasonably attributed to the polarization precursors dynamics occurring before para-ferroelectric phase transition in CBN alloys. Therefore, it can be considered that the total dielectric susceptibility is contributed by both lattice and precursor dynamics for $T_c < T < T_B$. The contribution of lattice dynamics to dielectric responses can be estimated from Curie law, here, we denote this part of dielectric susceptibility as χ'_{Curie} . The contribution of precursor dynamics to the dielectric response was then estimated by subtracting χ'_{Curie} from the total dielectric susceptibility χ' , and has the form of $\Delta\chi' = \chi' - \chi'_{\text{Curie}}$. The temperature variation of $\Delta\chi'$ is shown in Fig.7(a) and (c) for the two end compositions of CBN alloys. Upon cooling, $\Delta\chi'$ increases rapidly, for example, for $x = 0.32$, it increases from nearly zero at T_B to a large value that is about 34 % of the total dielectric response (2240) at T_c . For another end composition $x = 0.19$, precursor dynamics contributes approximately 25% of the total dielectric response at T_c . As shown in Fig.9(a), Ca-substitution enhances the contribution of precursor dynamics to the total dielectric response in CBN alloys.

Surprisingly, it was found that $\Delta\chi'$ increases exponentially upon cooling from T_B to T_c^+ . This can be clearly seen in Fig.7(c) where the y -axis was plotted in a logarithmic scale. The data of CBN alloys within the solid solution limit can be well analyzed by the following exponential law,

$$\Delta\chi' = \Delta\chi'_{T_c} e^{-k_B(T-T_c)/E_a} \quad (3)$$

where k_B is Boltzmann constant, $\Delta\chi'_{T_c}$ and E_a are constants. It should be noticed that the exponential law of dielectric response with temperature also has been observed in Pb-based ferroelectric oxides in our recent investigation.[48] The obtained parameters for equation (3) were shown in Fig.9(a) and (b).

From textbook, we know the relation of polarization P and dielectric susceptibility χ' ,

$$P = \chi' \epsilon_0 E, \quad (4)$$

where E is an electric field and ϵ_0 is the dielectric permittivity of vacuum. With the combination of this relationship and the exponential law shown in equation (3), it can be predicted that local polarizations grow exponentially upon cooling from T_B to T_c^+ in CBN alloys. Here, E_a is considered to be thermal activation energy required for the local polarization growth before transition into the ferroelectric phase. E_a was evaluated to be 2.2 meV \sim 3 meV for CBN alloys, which corresponds to a temperature of 25 K \sim 30 K. This barrier required for the precursor growth seems to be reasonable although there are no available data in the literatures to our knowledge.

We further used equation (4) to make an estimation of local polarization growing at $T = T_c^+$ using the very weak electric field ($E = 10^{-3}$ kV/cm) used in the dielectric measurements. The estimated values were given in Fig.9(c) as a function of composition x . At $T = T_c^+$, the local polarization is predicted to grow to a magnitude of 0.03 nC/cm² \sim 0.07 nC/cm² in CBN ceramics. Ca-substitution seems to enhance the local polarization growth in CBN alloys. This is reasonable since Ca-substitution reduces Curie point to a lower temperature, resulting in a larger temperature range ($T_c < T < T_B$) for the local polarization growth as shown in Fig.7(c) and Fig.10(a).

D. Phase diagram

Having discussed the thermal phase transition and the precursor behaviors in the above sections, we can establish a phase diagram for CBN alloys now. The proposed phase diagram was shown in Fig.10(a), in which the transition temperature T_c on cooling or heating was determined from the temperature dependence of dielectric susceptibility and T_B was estimated from deviation of Curie law in the dielectric susceptibility obtained upon cooling.

In our phase diagram, CBN alloys can be considered as paraelectrics with a centrocymetric tetragonal structure as that of isostructural compounds SBN for $T > T_B$. On cooling to $T \approx T_B$, polarization precursors emerge in the paraelectric mother phase of CBN alloys. On further cooling, these local polarizations growth exponentially with the temperature before transition into a ferroelectric phase with a non-centrocymmetric tetragonal structure

at $T = T_c$. This ferroelectric thermal phase transition is of first-order, and the transition temperature upon heating is $12.4 \sim 25.2$ K higher than that on cooling. As shown in the phase diagram, increase in Ca-concentration leads to a larger thermal hysteresis together with the lowering of T_c and T_B . On the other hand, the temperature range of precursor existence becomes larger as increasing the amount of substitution of smaller Ca ions for Ba ions. It is still unclear why Ca-substitution enlarges the precursor growth region, the local polarization developed at T_c^+ , and the thermal hysteresis of phase transition in CBN alloys. A likely reason is relative to the increase of vacancies in larger A_2 site in the TTB structure due to the increase of substitution amount of Ca for Ba. Because Ca almost exclusively occupied smaller A_1 site in CBN TTB structure, increase of Ca-concentration naturally results in the increase of vacancies in A_2 site occupied initially by Ba.[13, 14] Increase of vacancies in larger A_2 site with x may give rise to larger fluctuation of local lattice distortion in CBN alloys, which is though to be the sources of local polarizations. This suggestion is supported by recent investigations on the variation of lattice strain with x in CBN alloys, in which the thermal expansion along the polar axis becomes larger as increasing Ca-concentration.[22]

On the other hand, substitution of Ca for Ba leads to a nearly linear reduction of T_c and T_B with x . As well known in many normal ferroelectrics, pressure can significantly reduce the ferroelectric transition temperature. In solid solution, pressure can be due to chemical substitution of smaller ions for original larger one, and this kind of pressure is normally called as chemical pressure. Chemical-pressure effects on the reduction of T_c have been well studied in many ferroelectric alloys with perovskite structure such as $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$,[47] in which T_c -reduction is generally considered to be due to the reduction of unit cell volume by the chemical pressure effects. As mentioned in the above section, in CBN alloys, substitution of smaller Ca ions for Ba ions only lead to an extremely small change in its unit cell volume ($\Delta = (V(x) - V(0.19))/V(0.19)$), and Δ is less than 0.65% within the solid solution limit. Thus, it can be considered that the chemical pressure effects on the reduction of T_c was vanishingly small in CBN alloys.

The spontaneous polarization in CBN has been reported to be originated from Nb-displacement along the c -axis in the TTB structure.[13] It can be expected that the lattice distortion along the c -axis has influence on Nb-displacement. Figure 10(b) showed the variation of T_c with c -axis lattice constant. Indeed, one can see that T_c is reduced with the shrink of c -axis lattice. This fact indicates that the shrink of c -axis lattice should reduce the

space available for Nb-displacement, thus leading to the reduction of ferroelectricity and its T_c . However, since the reduction in c -axis lattice constant is approximately 0.03 Å within the solid solution, this lattice shrink is not enough to completely explain the large reduction in T_c in CBN alloys. It seems that other reasons may be existed for larger reduction of T_c with Ca-concentration in CBN alloys. The exact reason for this large reduction in T_c with Ca-substitution in CBN alloys remains to be clarified in further structural investigations.

IV. SUMMARY

In summary, we have studied the phase transition in CBN alloys within its solid solution limit ranging from $x = 0.19$ to $x = 0.32$. In contrast to their isostructural compounds SBN that normally show typical relaxor behaviors, CBN alloys exhibit behaviors such as normal ferroelectric BaTiO₃, but show precursors dynamics before transition into the ferroelectric phase. For $T > T_B$, CBN alloys obey classical Curie law and can be considered to be paraelectric. On further cooling toward T_c , local polarizations occurs in the paraelectric mother phase, and these polarization precursors grow exponentially as temperature lowering. Finally, a ferroelectric phase transition was realized at T_c . This thermal ferroelectric phase transition is essentially of first-order. A phase diagram was then establish for CBN ferroelectric alloys. These findings provide new insights on understanding the underlying physics in CBN ferroelectric alloys.

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FIG. 1: $(A_1)_2(A_2)_4(B_1)_2(B_2)_8O_{30}$ TTB structure of $Ca_xBa_{1-x}Nb_2O_6$ in projection along the polar c -axis, where A_1 , A_2 and B_1/B_2 sites are occupied by Ca, Ba and Ti ions, respectively.

FIG. 2: Powder X-ray diffraction patterns of $Ca_xBa_{1-x}Nb_2O_6$, which indicate that the ferroelectric solid solution has a limit of solid solution of $0.19 \ll x \ll 0.32$ beyond which single phase is not available.

FIG. 4: The dielectric susceptibility of $Ca_xBa_{1-x}Nb_2O_6$ polycrystals as a function of temperature and composition.

FIG. 5: Examples of frequency dependence of dielectric susceptibility and loss for $Ca_xBa_{1-x}Nb_2O_6$ polycrystals. It is clear that the transition temperature is not dependent on frequency and has a thermal hysteresis.

FIG. 6: Thermal phase transition in $Ca_xBa_{1-x}Nb_2O_6$ detected by differential scanning calorimetry (DSC). Exotherm or endotherm was seen during the phase transition as indicated by the arrows.

FIG. 7: (a) Examples of temperature variations of the measured dielectric susceptibility χ' , the fitting results by Curie law χ'_{Curie} (dashed lines), and their difference $\Delta\chi' = \chi' - \chi'_{Curie}$. (b) Inverse of the dielectric susceptibility χ' . The fitting results by Curie law are also shown by the dashed lines. Deviation from Curie law was seen from $T \approx T_B$ upon cooling. (c) Change of $\Delta\chi' = \chi' - \chi'_{Curie}$ plotted in a logarithmic scale for $T_c < T < T_B$. Dotted lines are the fitting results of an exponential law given in equation (3).

FIG. 8: Composition change of the fitting parameters used in Curie law (equation (2)) for the ferroelectric phase ($T < T_c$) and the paraelectric phase for $T > T_B$.

FIG. 9: (a) Composition change of $\Delta\chi' = \chi' - \chi'_{Curie}$ and $\Delta\chi'/\chi'$ at $T = T_c^+$. (b) Evaluated activation energy required for the local polarization precursors to grow in $T_c < T < T_B$ in the paraelectric mother phase. (c) Polarization growing at $T = T_c^+$, which was estimated by using equation (4) with the very weak field ($E = 10^{-3}$ kV/cm) used in the dielectric measurements.

FIG. 3: Change of lattice parameters of $Ca_xBa_{1-x}Nb_2O_6$ with composition.

FIG. 10: (a) Phase diagram proposed for $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ferroelectric alloys. In the shaded area, local polarizations were expected to grow exponentially with equation (3) within the paraelectric mother phase. FE=ferroelectric and PE=paraelectric. (b) Change of phase transition temperature with the polar c -axis lattice constant.

















